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Monolayer Formation Characteristics of Novel Organic Molecules with Nonlinear Optically Active Moieties

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A number of novel electroactive materials with amphiphilic molecular structure containing COOH, OH, NMe_2, OMe, NO_2 and CN were synthesized. This paper discusses the monolayer forming ability of these novel compounds. The stability of the monolayer as a function of pH, temperature, composition of the material in mixed monolayers and the nature of the subphase are investigated. Appropriate choice of experimental conditions under which a stable monolayer is obtained for each material is indicated. (AW)

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A - MONOLAYER FORMATION CHARACTERISTICS OF NOVEL ORGANIC MOLECULES WITH NONLINEAR OPTICALLY ACTIVE MOIETIES

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INTRODUCTION

Organic materials have recently been recognized as promising candidates for nonlinear optics (NLO) applications in view of their fast response time and large non-resonant nonlinear effects in comparison with their inorganic counterparts[1-3]. Novel organic materials that form molecular crystals and polymers with optimized molecular structure are therefore being synthesized and their NLO response assessed in attempts to obtain superior material performance. Another advantage of organic and polymeric materials is their relative ease of processing. It is possible to fabricate ultra thin films of organic NLO material that are suitably designed using the Langmuir-Blodgett (L-B) technique.

Using L-B technique it is possible to construct mono- and multilayers of organic compounds on a suitable substrate[4]. In so doing, precise control of the molecular organization and thickness (at nanometer levels) can be achieved. Optical properties of thin films, such as reflectance and transmittance depend, both on the thickness and complex index of refraction of a material. Both these parameters can typically be controlled in the L-B process. Possible applications of this technique are adequately covered in several reviews and special issues[5,6].

We recently reported[7] the design and synthesis of a class of organic compounds (Schiff base) possessing a large second order molecular hyperpolarizability, β. By attaching these quadratic NLO active groups to the

conjugated polymeric backbone such as polydiacetylenes (PDA's) we expect to obtain a unique material which is NLO active at both quadratic and cubic levels. PDA's have already been shown to possess one of the largest known non resonant cubic NLO susceptibility (χ^3) values[8,9]. We have synthesized a number of liquid crystalline quadratic NLO active compounds and their diacetylene derivatives. We report here a systematic study (using the L-B technique) on the monolayer forming ability of these novel compounds. In cases where they do form well defined monolayers, the stability of the monolayer obtained under different experimental conditions are investigated.

EXPERIMENTAL

The candidate materials used in this investigation were synthesized as per the scheme shown in Fig. 1a. Details of the synthetic procedures used will be published elsewhere[10]. The monolayer studies were carried out using a commercial Lauda film balance. To form monolayers, compounds dissolved in chloroform (1-2 mM concentration) were spread onto water at the desired pH or 10^{-4} M $CdCl_2$ solution as the subphase. A Millipore Milli-Q purification system was used for subphase preparation and a Lauda constant temperature bath was used to control the subphase temperature.

RESULTS AND DISCUSSION

The molecular structures of the candidate materials are shown in Fig. 1b. The molecular structures of the NLO active Schiff base compounds are indicted by M1, M2, M5 and M6. The surfactive compounds used in this study containing these functionalities are indicated by the roman numerals, I-VIII. Step 1 in Fig. 1a shows the synthetic route to the Schiff base compounds M1-M6. Steps 2 and 3 define the approach to the synthesis of the diacetylene compounds containing quadratic NLO groups. Step 4 is an intermediate stage for the synthesis of liquid crystalline compounds. I and II are intermediate compounds in our approach to

synthesize comb-like liquid crystalline polymers. The two materials contain M2 and M5 respectively as quadratic NLO active moieties which also function as mesogens. It is interesting to note that these materials themselves have been found to exhibit mesomorphic transitions and possess amphiphilic character as well, making them suitable for L-B monolayer formation. Compounds III and IV possess several interesting features: M2 and M5 as quadratic NLO active moieties; the diacetylene functionality for imparting cubic NLO activity through topochemical polymerization to a polydiacetylene; and amphiphilic character (carboxylic acid group).

The conventional approaches to render an organic compound nonlinear are to introduce strong electron donor and acceptor functionalities in its molecular structure: the NLO active moieties M1, M2, M5 and M6 possess this structural feature. We have introduced NO_2, CN, NMe_2 and OMe groups at one end of the molecule for this purpose. These groups are sufficiently polar to render them hydrophilic as well. In this sense, compounds I-IV contain surfactive groups at both ends of the molecule which introduce complications with respect to their alignment at the air-water interface. In order to understand the surfactive nature of these functionalities and to possibly resolve this "ambi-surfactive" character of molecules I-IV (through an appropriate choice of experimental conditions), compounds V-VIII were synthesized and subjected to L-B monolayer studies. The principal objective of this systematic study is to explore the conditions under which a stable L-B monolayer can be obtained for each molecule shown in Fig. 1. Results are summarized in Table I in which the appropriate combination of experimental conditions for obtaining a stable monolayer for each material is indicated.

Effect of subphase temperature: Isotherms were collected for all the materials shown in Table I as a function of temperature at the chosen pH. For

these materials we find that increasing temperature has a destabilizing effect on the monolayer stability (Fig. 2a). In general, the whole compression isotherm is shifted toward lower values of area/molecule on increasing the temperature (Fig. 2b). The upper limit on temperature in this study was 30° C because in many cases no monolayer was formed at or above this temperature. Many of our compounds exhibit interesting phase transformations during the course of monolayer formation. Significant shifts in these phase transitions are observed on changing the subphase temperature. This is illustrated in Fig. 2b for compound I. Phase transitions exhibited by this molecule probably indicate the different conformational arrangements adopted by the molecule at the air-water interface. Lowering the temperature has a stabilizing effect not only on the monolayer formed, but also on the intermediate phases during the process of monolayer formation. This in turn would lengthen the plateau region. This can be seen in Fig. 2b, where the plateau length gradually increases as the temperature is decreased.

Effect of subphase pH: Subphase pH has a remarkable effect on the nature of the monolayer formed. Owing to differences in the polarity of the hydrophilic head group across the spectrum of molecules (see Table I) used in this investigation, anchoring of these groups at the water surface can be influenced by changing the subphase pH. Desired pH was obtained by adding 1M solutions of either NaOH or HCl to the subphase. The effect of subphase pH on the compression isotherms for compounds V-VIII is quite dramatic and in fact, a monolayer did not form at all at neutral pH. The typical effect of subphase pH on the compression isotherm is illustrated for a representative compound VIII in Fig. 3. The actual pH range at which a reasonable monolayer is formed depends on the nature of the polar head group. In the case of compounds III and IV, however, subphase pH does not significantly change the monolayer formed.

This may be due to strong anchoring (on water) of highly hydrophilic COOH head group present in these compounds.

Miscellaneous effects: We have formed mixed monolayers of a few representative materials with classical monolayer forming compounds such as stearic acid and nonacosa-10, 12-diynoic acid. Typical isotherms obtained are represented in Figs. 4a and 4b, respectively. Our intention in this case is to determine the composition of the mixture for which a reasonable mixed monolayer can be obtained for the material under investigation. Compounds I and III by themselves exhibit low collapse pressure (see Fig. 2b) and large fluctuations in pressure during transfer on to solid substrates. In the mixed state however we see higher collapse pressures (Fig. 4a, 4b) and better monolayer stability during transfer.

For compounds III, IV and IX (containing carboxylic acid functionality as the hydrophilic head group) we find that using 0.1 mM solutions of $CoCl_2$ or $CdCl_2$ increased the stability of the monolayer formed.

CONCLUSION

We have synthesized several novel organic compounds in which structural units possessing large second and third order NLO response have been assembled together. Amphiphilic structural moieties have also been built in to these molecules to facilitate thin film processing by the L-B technique. Through a systematic study, we have identified the appropriate choice of experimental conditions (see Table I) to obtain a stable L-B monolayer for different classes of nonlinear optical materials possessing hydrophilic head groups of varying polarity. The linear and non-linear optical properties will be reported elsewhere.

ACKNOWLEDGEMENTS

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REFERENCES

1 D.S. Chemla and J. Zyss, eds., NLO Properties of Organic Molecules and crystals, Academic Press, Inc., New York, 1987.

2 D.J. Williams, ed., NLO Properties of Organic and Polymeric Materials, ACS Symp. Ser. 233, ACS, Washington, D.C., 1983.

3 P.N. Prasad and D.R. Ulrich, Nonlinear Optical and Electroactive Polymers, Plenum, New York, 1987.

4 G.L. Gaines, Insoluble Monolayers at Liquid-Gas Interfaces, Wiley, New York, 1966.

5 J.D. Swalen, J. Mol. Elec., Vol. 2, (1986) 155.

6 G.G. Roberts, Contemp. Phys. Vol. 25, No. 2, (1984) 109.

7 R.S. Kumar, J. Kumar, S.S. Kumar and A. Blumstein and S.K. Tripathy, MACRO 88 Proceedings, IUPAC Macromolecules, Kyoto, Japan, 1988, to be published.

8 G.M. Carter, Y.J. Chen and S.K. Tripathy in NLO Properties of Organic and Polymeric Materials, D.J.Williams, ed., ACS Symp. Ser. 233, ACS, Washington, D.C., 1983 p. 213.

9 G.M. Carter, Y.J. Chen, M.F. Rubner, D.J. Sandman, M.K. Thakur and S.K. Tripathy in ref. 1.

10 Organic Materials for Efficient Nonlinear Optics II. Synthesis and Characterization of Diacetylene Derivatives Containing NLO Active Moieties, To be submitted to Macromolecules.

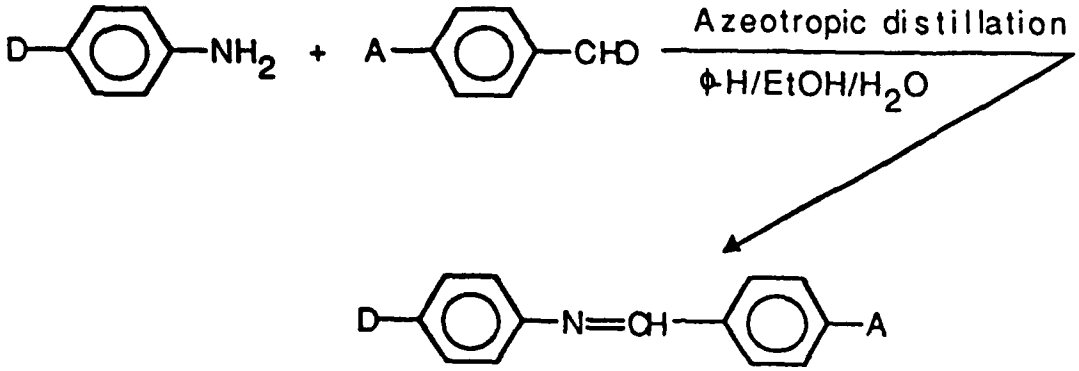
TABLE I. CONDITIONS FOR THE FORMATION OF STABLE MONOLAYER

COMPOUND NUMBER[a]	SURFACTIVE GROUP	CHOICE OF EXPERIMENTAL CONDITIONS			AREA/MOLECULE	
		pH	TEMPERATURE (°C)	SUBPHASE	CALCULATED (A^2/MOL)	ESTIMATED[b]
I	OH, NO_2	7	10.3	water	32.4	30.3
		10	20	water	32.7	
III	COOH, NO_2	7	10.3	water	24.1	23.5
IV	COOH, CN	-	12.5	$CdCl_2.H_2O$	32.04	33.6
V	NMe_2	3.8	12.5, 20	water	24.8	31.4
VII	CN	8.1	12.5, 20	water	29.2	30.3
VIII	OMe	7	12.5	water	40	36.6
		8.1	12.5, 20	water	38.6	

[a] compounds II, VI did not form satisfactory monolayers.

[b] estimated area of the molecule in its completely extended conformation.

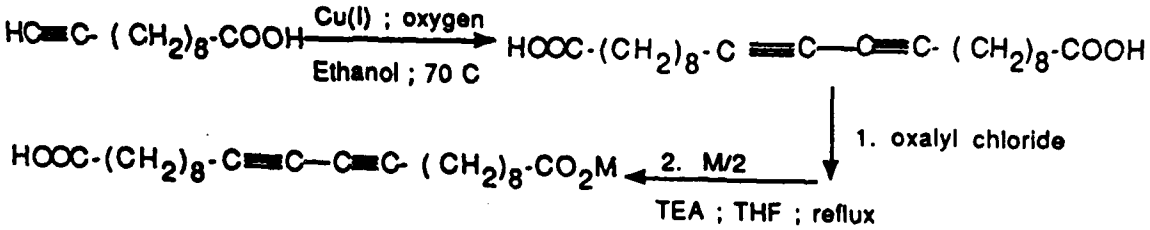
STEP 1:



[M]

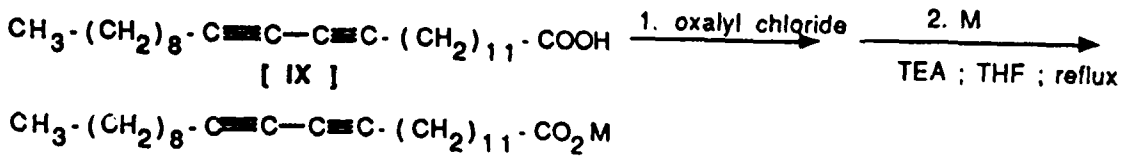
Aromatic Schiff base

STEP 2:



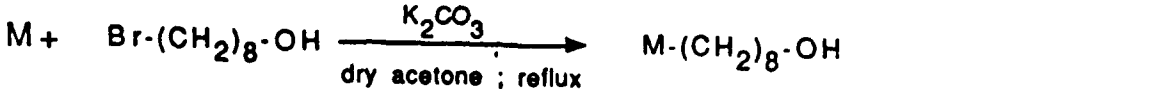
M = M2 [III] and M = M5 [IV]

STEP 3:



M = M1 [V] ; M = M2 [VI]
M = M5 [VII] and M = M6 [VIII]

STEP 4:



M = M2 [I] and M = M5 [II]

FIG 1a

FIG. 1a. SYNTHETIC SCHEME FOR THE PREPARATION OF THE COMPOUNDS INVESTIGATED.

MONOLAYER FORMATION CHARACTERISTICS OF NOVEL ORGANIC MOLECULES WITH NONLINEAR OPTICALLY ACTIVE MOIETIES

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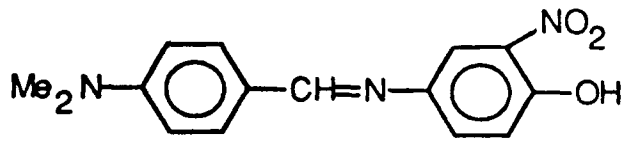
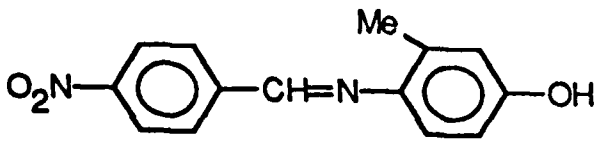
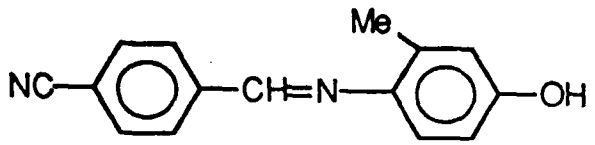


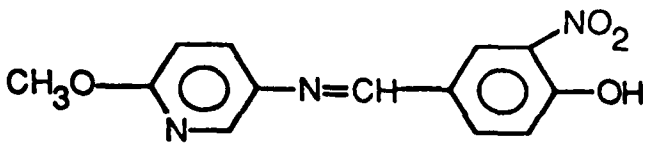
[M_1]



[M_2]



[M_5]



[M_6]

M-$(CH_2)_8$-OH

M = M2 [I] and M = M5 [II]

HOOC-$(CH_2)_8$-C≡C—C≡C-$(CH_2)_8$-CO_2M

M = M2 [III] and M = M5 [IV]

CH_3-$(CH_2)_8$-C≡C—C≡C-$(CH_2)_{11}$-CO_2M

M = M1 [V] ; M = M2 [VI]

M = M5 [VII] and M = M6 [VIII]

Fig 1b

FIG. 1b. MOLECULAR STRUCTURES OF THE COMPOUNDS INVESTIGATED; ROMAN NUMERALS REFER TO COMPOUND NUMBERS USED IN THE TEXT.

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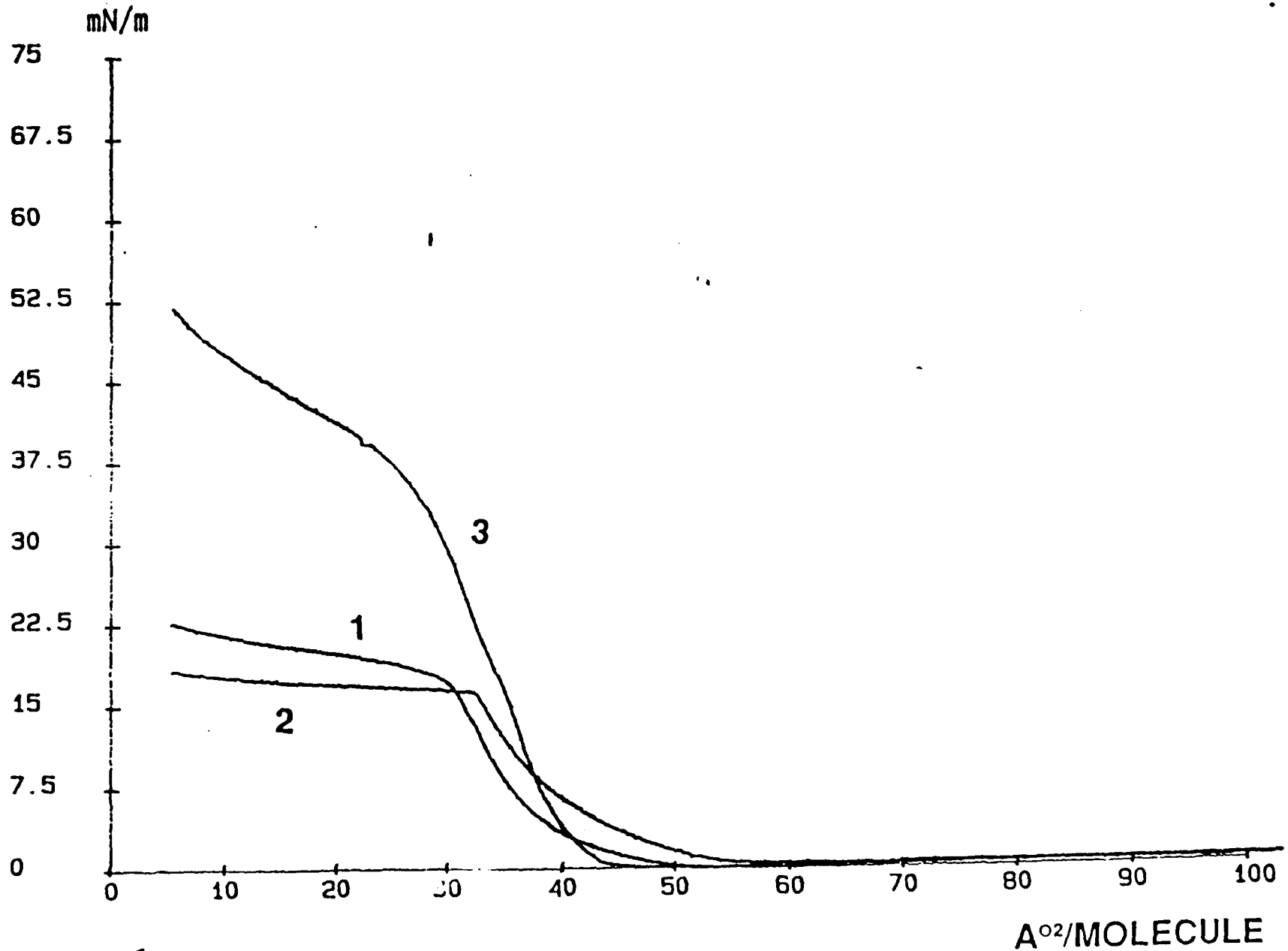
mN/m
75
67.5
60
52.5
45
37.5
30
22.5
15
7.5
0
0
10
20
30
40
50
60
70
80
90
100
A°2/MOLECULE
1
2
3

Fig. 2a

FIG. 2a. EFFECT OF TEMPERATURE ON THE MONOLAYER FORMATION OF COMPOUND VIII. 1: T=20°C; 2: T=30°C; 3: T=12.5°C

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FIG. 2b. EFFECT OF TEMPERATURE ON THE MONOLAYER FORMATION OF COMPOUND I. 1: T=10°C; 2: T=15°C; 3: T=20°C; 4: T=25°C

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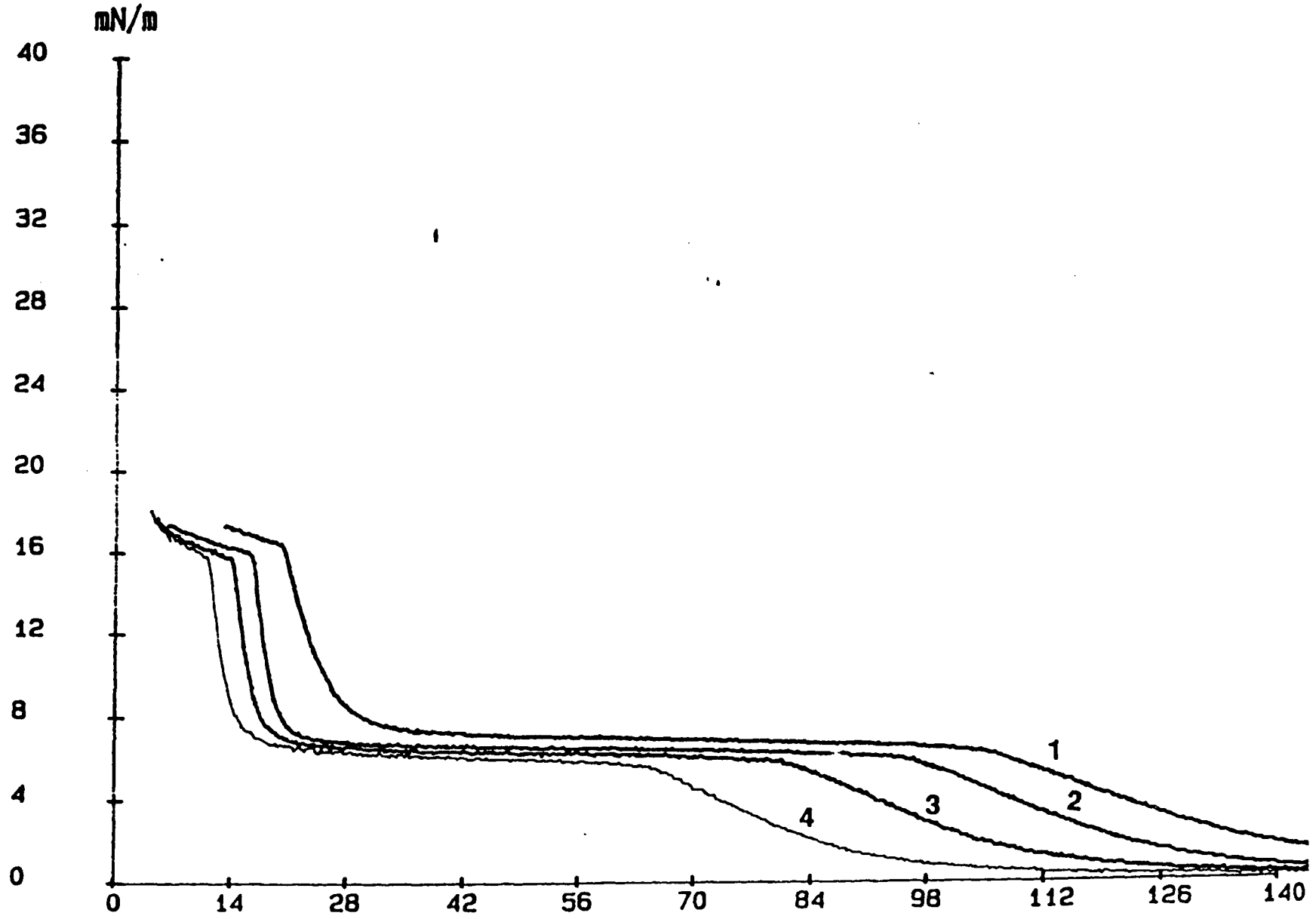
mN/m
40
36
32
28
24
20
16
12
8
4
0
0
14
28
42
56
70
84
98
112
126
140
1
2
3
4
A°2/MOLECULE

Fig 7b

FIG. 3. EFFECT OF SUBPHASE pH ON THE MONOLAYER FORMATION OF COMPOUND VIII. 1: pH 8.1; 2: pH 7; 3: pH 3.8

MONOLAYER FORMATION CHARACTERISTICS OF NOVEL ORGANIC MOLECULES WITH NONLINEAR OPTICALLY ACTIVE MOIETIES

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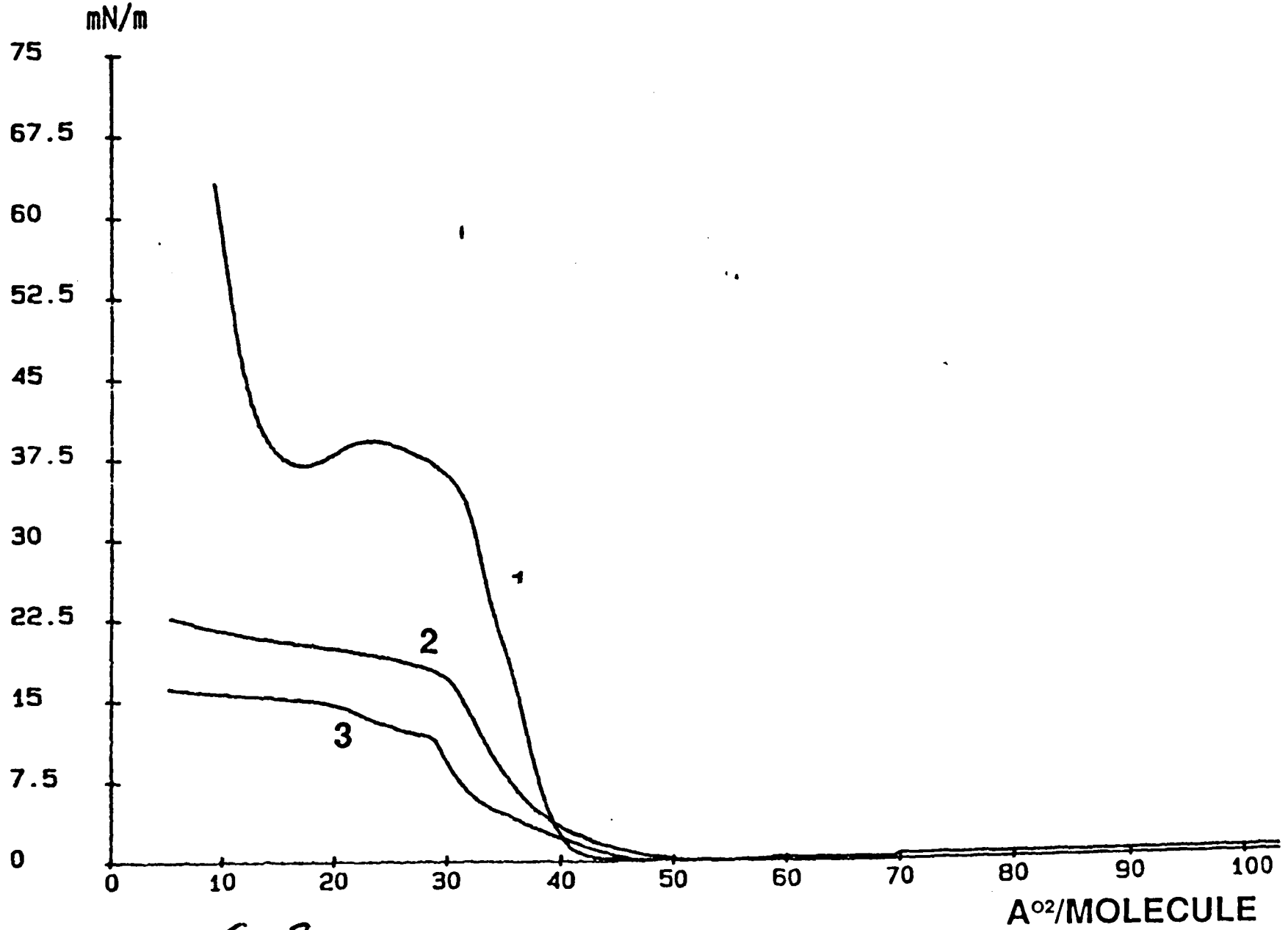
mN/m
75
67.5
60
52.5
45
37.5
30
22.5
15
7.5
0
0
10
20
30
40
50
60
70
80
90
100
A°2/MOLECULE
1
2
3

Fig. 3

FIG. 4a. MIXED MONOLAYER OF COMPOUND I WITH STEARIC ACID.

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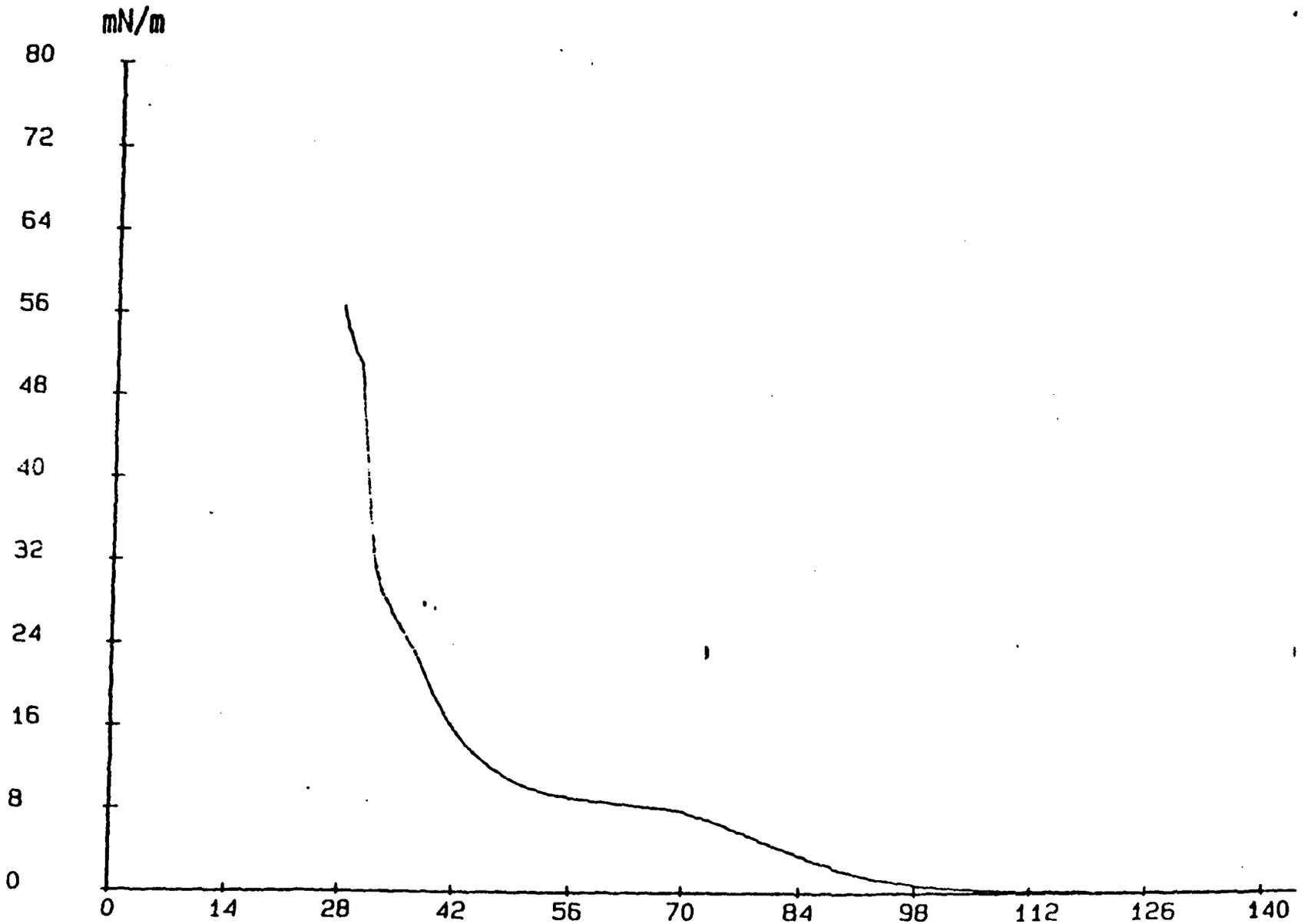
mN/m
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72
64
56
48
40
32
24
16
8
0
0
14
28
42
56
70
84
98
112
126
140
A°2/MOLECULE

Fig. 4a

FIG. 4b. MIXED MONOLAYER OF COMPOUND III WITH 10,12 NONACOSADIYNOIC ACID.

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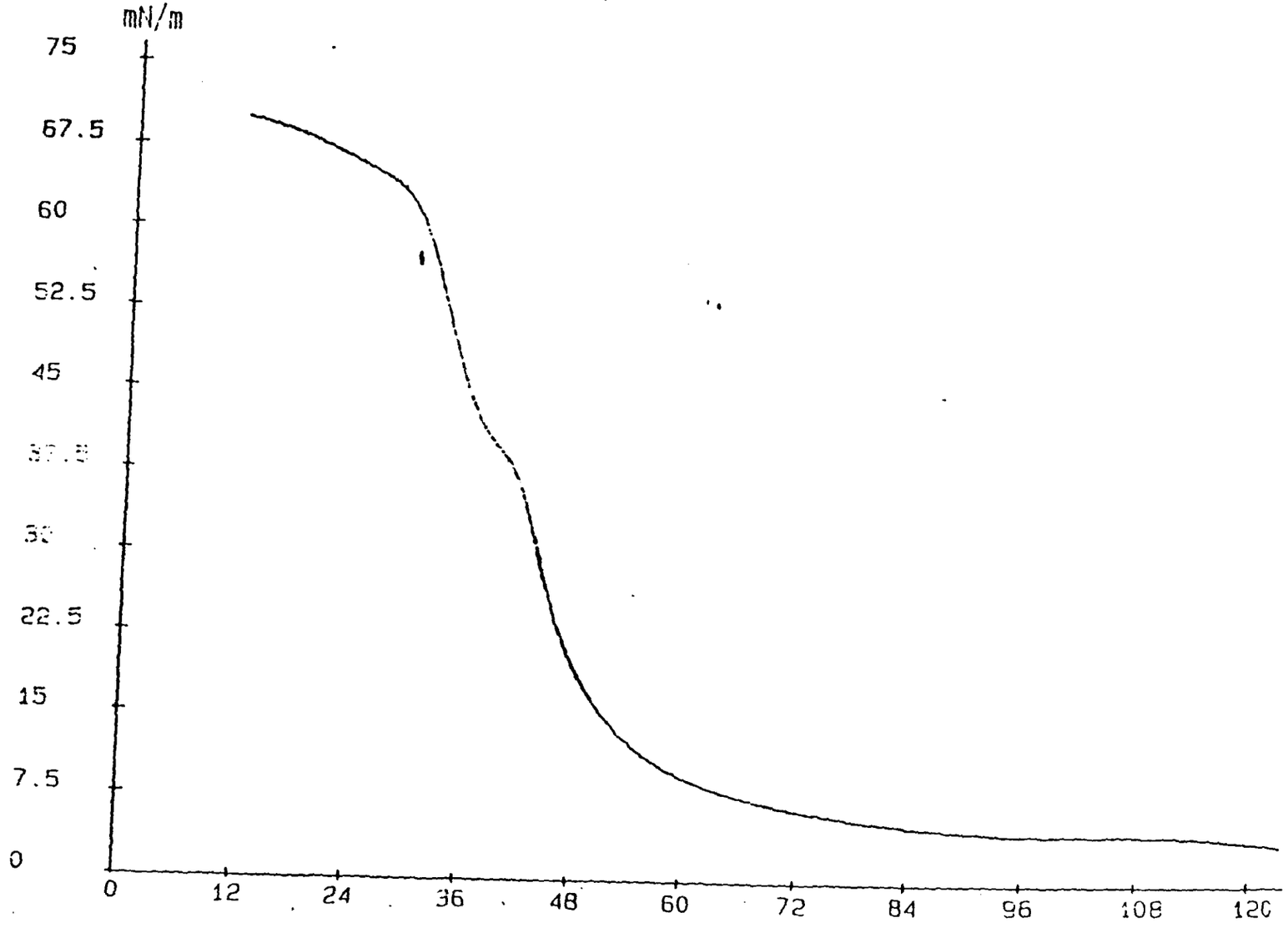

Fig 4h

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